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PALM OIL POLYOL/ POLYURETHANE SHAPE MEMORY NANOCOMPOSITES

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ABSTRACT

A series of nanoclay reinforced thermoplastic polyurethane with shape memory effect have been successfully synthesized via two-step polymerization process. The polyurethanes are composed of polycaprolactonediol, palm oil polyol, 4,4'-diphenylmethane diisocyanate and 1,4-butanediol. Nanoclay was added in order to improve the overall properties of the pristine polyurethane. Besides, the addition of palm oil polyol is believed to enhance the crosslinking process and further improve the properties. X-ray diffraction result showed that there is a decrease in crystallinity of polyurethane nanocomposites as clay is added. Good shape memory and mechanical properties of resulting polyurethane nanocomposites were obtained in this work.

Keywords: clay; palm oil polyol; polyurethane; shape fixity; shape recovery

INTRODUCTION

Polyurethane can be found in many forms such as adhesive, foam, coating, elastomers etc. and it covers wide range of applications from household appliances to aircraft parts owing to its versatility characteristics. The most advanced application of polyurethane is in the field of intelligence or smart materials as shape memory polymer. The shape memory polyurethane has the ability of changing shape upon application of external stimulus. The shape memory effect is induced due to the existence of two separated phases of polyurethane owing to the non-homogeneity of soft and hard segment domains.

Polyurethane from polyester polyol is known to be more biodegradable as compared to polyether polyol. Hence, polycaprolactonediol is consumed to form soft segment domains in this work. In addition, a renewable resource, palm oil polyol is introduced due to its easy availability and low cost. On top of that, the call for environmental preservation and awareness had urged the use of palm oil polyol as it is totally environmental friendly. It is believed that the presence of large number of surface

functionality due to the hyperbranched structure of palm oil polyol could help in mixing process and enhance the interactions between precursors [1].

Particularly, nanoclay has been used as filler in polymer for sometime due to its stiffness and high aspect ratio. The addition of nanoclay could enhance the thermal stability, gas barrier and mechanical properties of the resulting composite as compared to the pristine polymer. In this work, Cloisite 30B which is reactive nanoclay is chosen as filler in order to improve the properties of shape memory polyurethane produced. The characterization includes X-ray diffraction, mechanical and shape memory tests.

EXPERIMENTAL DETAILS

Materials and Method

Polyurethane prepolymer was first synthesized via two-step polymerization process according to modified procedure of Jana *et al.*[2] which involved the reaction of 4,4-diphenylmethane diisocyanate (MDI, Sigma Aldrich) and polycaprolactonediol (PCL, Perstorp Polyols, UK, MW=4000 g/mol) for 30 min at 80 °C. Then, palm oil polyol (Rovpol 1100, Rovski Sd. Bhd., MW=900 g/mol) was added and further mixed for another 2.5 hr with a stirring speed of 500 rpm. MDI was used as received while PCL and palm oil polyol were dried overnight in an oven at 45 °C before synthesis. The reaction took place in a 500 ml three-neck round bottom flask held in an oil bath and surrounded with N_2 atmosphere. The feed molar ratio of PCL/palm oil polyol/MDI/BD was kept constant at 0.8/0.2/6/5. In the second step, the prepolymer, 1,4-butanediol (BD, Sigma Aldrich) and nanoclay (Cloisite 30B, Southern Clay Products) were added into Brabender internal mixer and mixed for 15 min at 90 °C. The added clay was varied at 1, 3 and 5 wt% and it was dried overnight in oven at 100 °C prior to use. Few drops of dibutyltin dilaurate (DBTDL, Sigma Aldrich) catalyst were added to pristine polyurethane sample only.

The produced polyurethane was first dried in oven at 80 °C for 2 hr before pressed using compression molding at temperature of 150 °C. The final samples were in the form of rectangular sheets with thickness of 0.5 mm.

Characterization

X-ray diffraction measurements were collected using X-ray diffractometer (Siements D 500). The diffraction was recorded at a scan rate of 1°/min between 10 to 30° range of 2θ.

The study of shape memory behavior of the samples was determined by bending a rectangular sheet at temperature of 60 °C and forming a ring-like shape (temporary shape). The ring shaped sample was then rapidly cooled to 3 °C by putting in an ice-water bath for 10 min. The deforming stress was released and an immediate change in angle was measured as constraint removal angle, θ_{cr}. In the final step, the sample was heated back to 60 °C and the final angle, θ_f was measured. The method is compliant with a method proposed by Rana *et al.* [1]. The shape fixity and shape recovery of the samples are considered according to formula below:

Shape fixity (%) = θ_{cr} / 90° × 100. (1)
Shape recovery (%) = (90° - θ_f) / 90° × 100. (2)

The mechanical properties of the samples were measured using Universal Testing Machine model Instron 5567 at room temperature using 1 kN load cell. The samples were cut into dumbbell-shaped specimens with dimensions according to ASTM D638-type V. The strain rate and gauge length were 50 mm/min and 25 mm respectively.

RESULTS AND DISCUSSION

The XRD data are presented in order to study the crystallization behavior of SMPU since it is one of the important measures in fixing the temporary shape. Figure 1 shows the X-ray diffraction pattern for SMPU in which the existence of two peaks at 21.3° and 23.6° denotes the presence of PCL crystals corresponding to (110) and (200) planes, respectively [3]. As one can see, the peak height decrease with increasing clay content indicates the decrease in PCL crystallinity upon clay addition. It suggests that the presence of clay hindered the chains mobility and thus interrupt their ability to pack into crystalline structure.

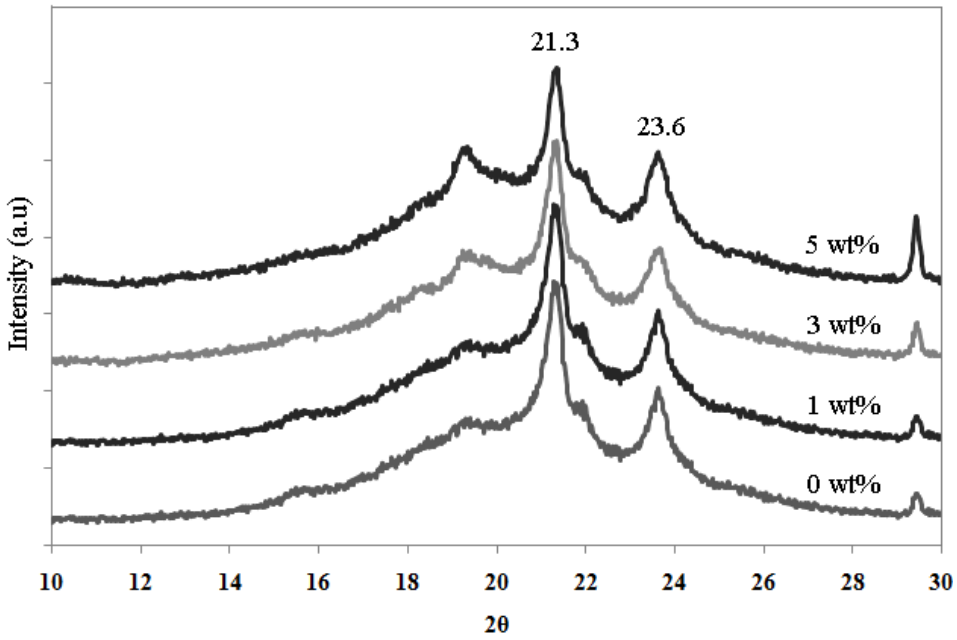

Figure 1: X-ray diffractogram of SMPU

The shape memory behavior of pristine SMPU and SMPU filled clay can be observed in Figure 2. The value of shape fixity and shape recovery remains 100% in SMPU with 3 wt% clay content. In 5 wt% clay content, the values decreased. The shape fixity depends mainly on the ability of the SMPU to crystallize during cooling and fixed the temporary shape. The lacks of adequate amount of crystalline phase cause the immediate shrinkage upon releasing of deforming stress. This may be due to excess

clay content that disturbs the crystallization process. On the other hand, the permanent shape depends mainly on the physical crosslinks attributed by the dipole-dipole interactions and hydrogen bonding in the SMPU system. The decrease in shape recovery may be due to decrement in the degree of physical crosslinking in presence of excess clay [4].

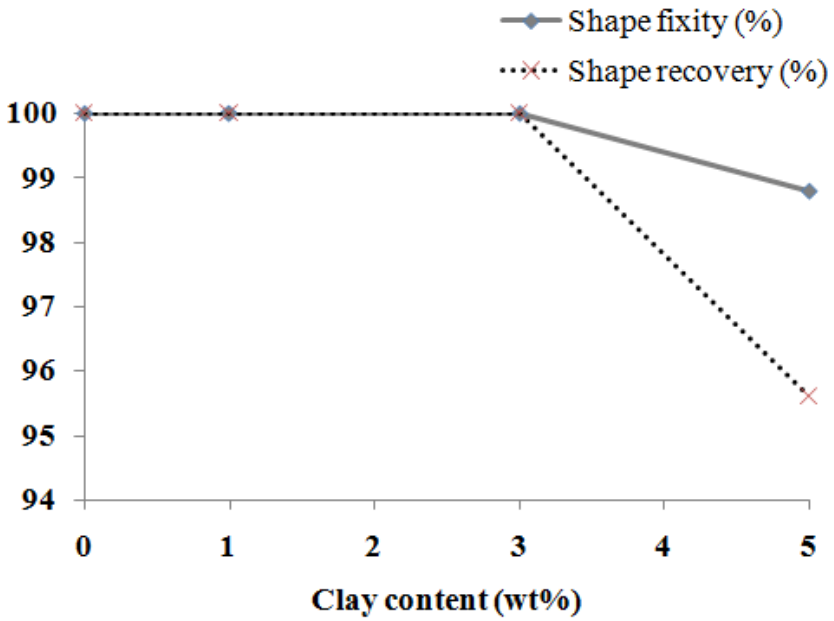

Figure 2: Shape memory properties of SMPU

Figure 3 shows the variations of modulus, stress and strain at break for pristine SMPU and SMPU filled clay. The introduction of nanoclay filler in polyurethane system had promoted better physical crosslinking due to polymer-filler interactions occurred in the nanocomposites. The modulus showed an increasing trend with increasing clay content. The same trend is observed for stress and strain at break in which the value is increased up to 3 wt% clay addition. However, the decrement of the value in 5 wt% filled clay may be due to the existence of excessive clay that restrain the formation of physical crosslinks and therefore promote the mixing of soft segment and hard segment phases.

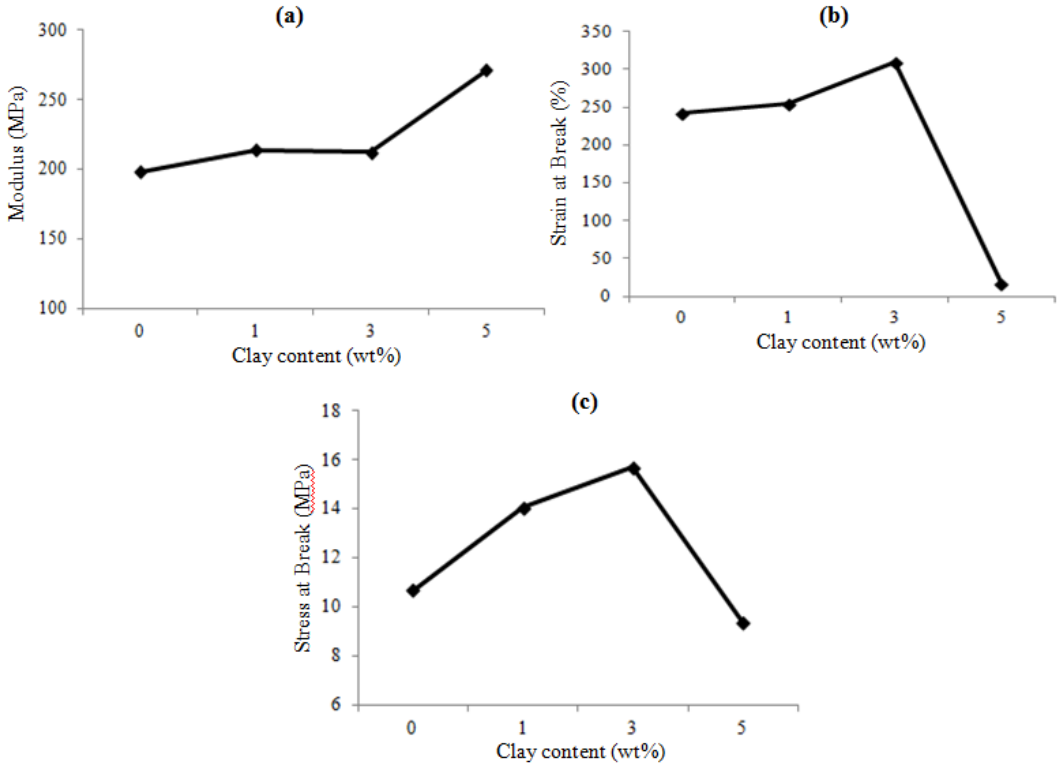

Figure 3: (a) Modulus, (b) strain at break and (c) stress at break of the SMPU nanocomposites

CONCLUSION

A set of SMPU filled nanoclay was studied in this work. The results obtained demonstrate good shape memory behavior upon addition of clay up to 3 wt%. The good shape fixity was owing to the formation of crystalline soft segment domains during cooling while the good shape recovery was due to the interactions between clay and hard segment domains that enhanced the physical crosslinking and thus allow the recovery of permanent shape. In addition, the good interface interactions between clay and polyurethane matrix had improved the mechanical properties of SMPU.

ACKNOWLEDGEMENT

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